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The first four-membered ring compound containing two gallium atoms bridged by two different Group 15 elements, $I_2\overline{GaAs(SiMe_3)_2Ga(I)_2P}(SiMe_3)_2$ (**1**) to be completely characterized wassynthesized by both the equilibration of $[I_2GaAs(SiMe_3)_2]_2$ (**2**) and $[I_2GaP(SiMe_3)_2]_2$ (**3**) in a 1:1 mole ratio, and the direct reaction of GaI_3 with $As(SiMe_3)_3$ and $P(SiMe_3)_3$ in a 2:1:1 mole ratio. Single crystal x-ray structures were determined for both **1** and **3**. Crystals of **1** belong to the orthorhombic system, space group *Pbca*, with $a = 17.349(3)$, $b = 13.9187(21)$, $c = 13.7570(24)$ Å, $V = 3322.0(10)$ Å^3, $D_{calc} = 1.879$ g cm^{-3} for $Z = 4$; the average Ga-As/P bond length is 2.44 Å, and crystals of **1** are isomorphous with those of **2**. Crystals of **3** belong to the monoclinic system, space group $P2_1/c$, with $a = 11.040(9)$, $b = 10.228(4)$, $c = 19.619(9)$ Å, $V = 2169.4(22)$ Å^3, $D_{calc} = 1.816$ g cm^{-3} for $Z = 4$; the average Ga-P bond length is 2.39 Å.

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Abstract

The first four-membered ring compound containing two gallium atoms bridged by two different Group 15 elements, $\overline{I_2GaAs(SiMe_3)_2Ga(I)_2P}(SiMe_3)_2$ (**1**) to be completely characterized was synthesized by both the equilibration of $[I_2GaAs(SiMe_3)_2]_2$ (**2**) and $[I_2GaP(SiMe_3)_2]_2$ (**3**) in a 1:1 mole ratio, and the direct reaction of GaI_3 with $As(SiMe_3)_3$ and $P(SiMe_3)_3$ in a 2:1:1 mole ratio. Single crystal x-ray structures were determined for both **1** and **3**. Crystals of **1** belong to the orthorhombic system, space group *Pbca*, with a = 17.349(3), b = 13.9187(21), c = 13.7570(24) Å. V = 3322.0(10) Å^3, D_{calc} = 1.879 g cm^{-3} for Z = 4; the average Ga-As/P bond length is 2.44 Å, and crystals of **1** are isomorphous with those of **2**. Crystals of **3** belong to the monoclinic system, space group $P2_1/c$, with a = 11.040(9), b = 10.228(4), c = 19.619(9) Å, V = 2169.4(22) Å^3, D_{calc} = 1.816 g cm^{-3} for Z = 4; the average Ga-P bond length is 2.39 Å.

Introduction

The quest for single-source precursors to binary 13-15 compound semiconductors has led to the discovery of many novel compounds of varying structures and compositions.[1,2] This search has been recently expanded to include precursors to ternary 13-15 compound semiconductors, although few successful accounts of such species have been recorded to date. Cowley, *et al*, have reported NMR evidence for a mixed-metal complex of formula $Me_2GaP(^tBu)_2InMe_2P(^tBu)_2$, however no detailed structural information was reported for this complex.[3] Previous attempts to prepare ternary 13-15 compounds in our laboratory have proven difficult, as direct syntheses of such compounds from binary 13-15 precursors often yielded binary ligand rearrangement products instead of the desired ternary compound.[4,5]

Recently, we reported the isolation of the four-membered In-As-In-P ring compound $(Me_3SiCH_2)_2InAs(SiMe_3)_2In(CH_2SiMe_3)_2P(SiMe_3)_2$ by the equilibration of the corresponding dimeric In-As and In-P compounds $[(Me_3SiCH_2)_2InAs(SiMe_3)_2]_2$ and $[(Me_3SiCH_2)_2InP(SiMe_3)_2]_2$.[5,6] This In-P compound was shown to undergo a monomer-dimer equilibration in solution, which provided a pathway for recombination of the monomeric units into the mixed-pnicogen complex. A similar monomer-dimer equilibrium has also been seen for both the gallium-containing species $[I_2GaAs(SiMe_3)_2]_2$[7] and $[I_2GaP(SiMe_3)_2]_2$;[8] thus it would be expected that when these two are combined in solution and allowed to equilibrate, a mixed-pnicogen Ga-As-Ga-P complex would result.[5]

Herein we report the synthesis and characterization of the mixed-pnicogen complex $I_2GaAs(SiMe_3)_2Ga(I)_2P(SiMe_3)_2$ (**1**) by both the solution equilibration of $[I_2GaAs(SiMe_3)_2]_2$ (**2**) and $[I_2GaP(SiMe_3)_2]_2$ (**3**), and the direct reaction of GaI_3 with $As(SiMe_3)_3$ and $P(SiMe_3)_3$. The crystal structure of (**3**), previously unreported,[8] is also detailed.

Results and Discussion

The reaction of equimolar amounts of **2** and **3** in toluene at room temperature produced a yellow powder which was found to be a mixture of **2** and **3**, with no crystalline product obtained.

As a crystalline product was described in the formation of the similar In-As-In-P ring compound $(Me_3SiCH_2)_2InAs(SiMe_3)_2In(CH_2SiMe_3)_2P(SiMe_3)_2$ (**4**),[6] it was deduced that the reaction to form **1** was not proceeding to completion at room temperature. In an attempt to drive the reaction to the desired product **1**, a solution similar to the one previously described was sealed in a flask and placed in a sonicating cleaning bath for 2 days. The product of this reaction was also a yellow powder identified as a mixture of **2** and **3**, with no crystalline product. When a solution of equimolar amounts of **2** and **3** in toluene remained in the sonicating cleaning bath for 4 days, a yellow-brown powder resulted, from which was grown X-ray quality crystals of **1**.

Crystallographic studies of **1** revealed arsenic and phosphorous in a 50/50 ratio of occupation at the pnicogen sites. An exact identification of a P or As at the individual pnicogen sites was not possible; as the planar four-membered ring of **1** lies along a C_2 symmetry axis, a feature shared with both **2** and **3**. From these observations, two possibilites were determined for crystals of **1**: **1** could be a single molecule with disorder on the two-fold axis preventing resolution of the pnicogen sites; or **1** could be an exact co-crystallization of **2** and **3**, with disorder resulting from the P and As occupying the pnicogen site in a 50/50 ratio. Data collected for the structure of **4** indicated that an average of crystallographic values from the starting materials would be expected for a mixed-pnicogen complex.[6] The structure of **1** (Figure 1, Tables 1 and 2) did exhibit many similarities with those of the starting materials **2** (reference 7) and **3** (Figure 2, Tables 1 and 3), but very seldom corresponded to an exact average of the crystallographic values observed for those compounds. Deviations from the values expected in the case of **1** was likely a result of the structure of **3**, which is solvated by two toluene molecules per dimeric unit, with the methyl groups pointing into the four-membered Ga-P-Ga-P ring. Crystals of **1** and **2** belong to the orthorhombic space group *Pbca*, in contrast with **3** which belongs to the monoclinic space group $P2_1/c$. Unit cell parameters found for **1** (a = 17.3 Å, b = 13.9 Å, c = 13.8 Å) corresponded well with **2** (a = 14.3, b = 17.5, c = 13.9), but differed greatly with those for **3** (a = 11.0, b = 10.2, c = 19.6). The average bond lengths between the metal and pnicogen sites in **1** (2.44 Å) are close to the average of those seen for **2** (2.47 Å) and **3** (2.40 Å). Bond angles observed at the E-

Ga-E' and Ga-E-Ga' sites for **1** (92.2°, 87.8°, respectively) were nearly identical to those of **2** (92.0°. 88.0°) and **3** (92.2°, 87.8°). Likewise, the I-Ga-I and average Ga-E-Si bond angles for **1** (104.3°, 113.6°, respectively) were also similar to those measured for **2** (105.4°, 113.9°) and **3** (104.5°, 114.1°). As a result of these anomolies in the crystal structure, further analysis was needed to confirm this compound as having the structure proposed as **1**.

Mass spectra were run using the electron ionization method on two different samples of **1**. A sample of bulk powder shows a clear parent ion peak at 1044.2 *m/z*, however both **2** and **3** are present as well, with peaks at 1002.1 and 1090.4, respectively. The spectrum of a crystalline sample of **1** shows only the expected $(M + H)^+$ peak at 1045.2, and no peaks for the starting materials. Only a small amount of pure crystalline **1** was obtainable from the bulk powder, therefore another method of synthesizing **1** was needed.

To this end, a pentane solution of $As(SiMe_3)_3$ and $P(SiMe_3)_3$ was added to a stirred pentane slurry of GaI_3. This mixture was then sealed in a flask and set in a sonicating cleaning bath, during which time a white precipitate formed. Crystals suitable for X-ray structural study were grown from a toluene solution of this precipitate, and were verified by unit cell determination as being **1**. ^1H NMR of this sample showed a singlet at δ 0.54 ppm and a doublet centered at δ 0.33, which correspond to the protons on the silyl groups of the arsenic and phosphorus atoms, respectively. The absence of the triplet/doublet pattern expected for **3** in this spectrum corresponded with that seen previously for **4**,[6] confirming that only one phosphorus is present in the ring system of **1**, and that it remains largely intact in solution. Some small sidebands were noticeable on either side of the singlet, and could correspond to some recombination of monomeric $I_2GaP(SiMe_3)_2$ units in solution to form **3**. ^{13}C NMR of the same sample displayed a singlet at δ 3.23 and a doublet centered at δ 2.25, corresponding to the carbons on the silyl groups of the arsenic and phosphorus atoms, with the carbons attached to the phosphorus being split into a doublet. This also agrees with the data presented for **4** as evidence of one As and one P present in the ring of **1**. ^{31}P NMR of **1** showed a singlet at δ -261.25 ppm. Since only a singlet is present, it can be safely concluded that only **1** is present in this sample.

Preliminary decomposition studies on the sample of **1** obtained from the direct preparation have been encouraging as to obtaining $Ga_xAs_yP_{(1-y)}$ from this precursor. Thermo-Gravimetric Analysis/Differential Thermal Analysis (TGA/DTA) data (Figure 3) indicated that four moles of trimethylsilyliodide (by weight) were eliminated from **1** when it was heated to 400 °C under vacuum. The remaining weight percentage at 400 °C (16.74%) was less than that expected for the Ga_2AsP core of **1** (23.46%); however, some weight was lost from the sample before the thermal analysis began, as evidenced from the starting point of the spectrum at 91.06%. When the spectrum is normalized to begin at 100% weight, the remaining weight at 400 °C becomes 25.68%, which corresponds well with the aforementioned percentage for the core of **1**. An X-ray powder diffraction spectrum (Figure 4) of a sample of **1** thermally decomposed in a similar manner was shown to be crystalline, with a broad peak identified in the region expected for the (111) reflection for 13-15 compound semiconductors. The *d*-spacing value of this peak (3.23 Å) was between those published as standards for GaAs (3.26 Å)[14] and GaP (3.14 Å)[15], and thus could be indicative of a material containing interstitial GaAs and GaP bonds. Further investigation into the decomposition behavior of **1** is continuing in our laboratories on the basis of these results.

Experimental Section

General Considerations. All manipulations were performed using Schlenk and/or dry box techniques. Solvents were appropriately dried and distilled under dry dinitrogen prior to use. Literature methods were used to prepare $[I_2GaAs(SiMe_3)_2]_2$,[7] $[I_2GaP(SiMe_3)_2]_2$,[8] $As(SiMe_3)_3$,[9] and $P(SiMe_3)_3$.[10] GaI_3 (99.999% purity) was purchased from Alfa/Johnson-Matthey, and used as received. Single-crystal X-ray diffraction data were collected at -170 °C on a Rigaku AFC6/S diffractometer using the omega scan mode, and graphite-monochromated Mo-$K\alpha$ radiation. Crystallographic data was refined using the NRCVAX[11] System at the University of North Carolina at Chapel Hill Single Crystal X-Ray Facility. ^1H, ^{13}C, and ^{31}P NMR were obtained on a Varian XL-300 (300, 75.4, and 121.4 MHz, respectively) spectrometer using sealed 5-mm tubes. ^1H and ^{13}C were referenced to tetramethylsilane using the residual protons or carbons of

deuterated benzene at δ 7.15 or 128 ppm. ^{31}P NMR spectra were referenced externally to H_3PO_4 at δ 0.00 ppm. Mass spectra were collected on a JEOL JMS-SX 102A spectrometer operating in the electron ionization mode at 20 eV. Thermo-Gravimetric Analysis/ Differential Thermal Analysis (TGA/DTA) data was collected on a TA Instruments SDT 2960 simultaneous DTA/TGA instrument. X-ray powder diffraction (XRD) studies were performed on a Phillips XRG 3000 diffractometer using Cu-$K\alpha$ radiation (λ = 1.5418 Å; graphite monochromator). Elemental analyses were run by E + R Microanalytical Laboratory, Corona, NY.

Synthesis of (1) by equilibration of (2) and (3). $[I_2GaAs(SiMe_3)_2]_2$ (0.326 g, 0.299 mmol) and $[I_2GaP(SiMe_3)_2]_2$ (0.300 g, 0.299 mmol) were both placed in a 250-mL screwtop reaction flask equipped with a Teflon valve and dissolved in 125 mL of toluene. The solution was slightly yellow after dissolution was complete. The flask was sealed and set in a sonicating cleaning bath for 4 days. During this time, the solution turned cloudy orange-brown with a fine brown powder settling out at the base of the flask. The solvent was removed *in vacuo* to yield a yellow-brown powder, which was subsequently collected and washed in pentane. Crystals suitable for X-ray structure determination were grown from toluene at -15 °C in a Dri-Lab refrigerator. Yield of (**1**): 0.020 g (0.019 mmol, 6.4% based on As and P). The electron ionization (20 eV) mass spectrum shows a cluster for $(C_{12}H_{37}AsGaI_4PSi_4)^+$ at *m/z* 1047, corresponding to the expected $(M + H)^+$ peak for (**1**).

Synthesis of (1) from GaI_3, $As(SiMe_3)_3$, and $P(SiMe_3)_3$. GaI_3 (0.500 g, 1.11 mmol) was placed in a 300 mL screwtop reaction flask equipped with a Teflon valve, and 50 mL of pentane was then added. $As(SiMe_3)_3$ (0.164 g, 0.556 mmol) and $P(SiMe_3)_3$ (0.140 g, 0.556 mmol) were combined in a vial and dissolved in 30 mL pentane. This solution was added *via* pipet to the stirring slurry of GaI_3/pentane. Upon completion of addition, the solution was cloudy and white, with unreacted GaI_3 at the base of the flask. The flask was sealed and set in a sonicating cleaning bath for 1 day. After ca. 5 minutes of sonication, the entire mixture turned white, with no trace of unreacted GaI_3. The solvent was removed *in vacuo* to reveal a yellow-white powder,

which was collected to yield 0.580g (0.555 mmol, 99.8% yield based on As and P). Anal. Calcd. (Found) for $C_{12}H_{36}AsGa_2I_4PSi_4$: C, 13.78 (14.07); H, 3.47 (3.51); As, 7.16 (7.44); Ga, 13.33 (13.61); I, 48.54 (48.21); P, 2.96 (2.84). ^{1}H NMR (C_6D_6): δ 0.54 (s, AsSi*Me3*), 0.34 (d, PSi*Me3*). ^{13}C NMR (C_6D_6): δ 2.30 (d, Si*Me3*). ^{31}P NMR (C_6D_6): δ -261.25 (s, *P* SiMe3). Crystals suitable for X-ray structure determination were grown from toluene in a -15 °C Dri-Lab refrigerator.

X-ray structural solution and refinement. Crystallographic data are summarized in Table I. The crystals of **1** and **3** used were colorless blocks which were mounted separately on glass fibers with a viscous oil under a stream of cold dinitrogen. X-ray intensity data were recorded at -170 °C, and the structures were solved by direct methods. Full-matrix least-squares refinement with weights based upon counter statistics was performed. Hydrogen atoms were incorporated at their calculated positions using a riding model in the later iterations of refinement which converged at R = 0.031 (R_w = 0.038) for **1** and R = 0.032 (R_w = 0.036) for **3**. A final difference-Fourier synthesis revealed no unusual features (max. 0.600, min. -0.650 e Å^{-3} for **1**; max. 0.820, min. -0.680 e Å^{-3} for **3**). Crystallographic calculations were performed using the NRCVAX[11] suite of structure determination programs. For all structure-factor calculations, neutral atom scattering factors and their anomalous dispersion corrections were taken from Ref. 12. Interatomic distances and angles are given for **1** in Table II and for **3** in Table III. ORTEP[13] diagrams showing the solid state conformation and atom numbering scheme of **1** and **3** are presented in Figures 1 and 2, respectively. Full information concerning conditions for crystallographic data collection and structure refinement, atomic coordinates, thermal and positional parameters, and observed and calculated structure factors has been deposited with the Cambridge Crystallographic Data Center.

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(15) JCPDS File #12-191.

Table 1. Crystallographic Data and Measurements for $I_2GaAs(SiMe_3)_2Ga(I)_2P(SiMe_3)_2$ (**1**), and $[I_2GaP(SiMe_3)_2]_2$ (**3**).

	(1)	(3)
molecular formula	$C_{12}H_{36}AsGa_2I_4PSi_4$	$C_{26}H_{52}Ga_2I_4P_2Si_4$
formula weight	1045.70	1186.04
crystal system	orthorhombic	monoclinic
space group	*Pbca*	$P2_1/c$
a (Å)	17.349(3)	11.040(9)
b (Å)	13.9187(21)	10.228(4)
c (Å)	13.7570(24)	19.619(9)
V (Å^3)	322.0(10)	2169.4(22)
Z	4	4
D_{calcd} (g cm^{-3})	1.879	1.816
radiation (wavelength, Å)	Mo-$K\alpha$ (0.71073)	Mo-$K\alpha$ (0.71073)
μ, (mm^{-1})	6.48	4.33
temp (°C)	-170	-170
crystal dimensions (mm)	0.30 x 0.26 x 0.20	0.35 x 0.30 x 0.25
T_{max};T_{min}	0.2592; 0.1402	0.3946; 0.1688
scan type	ω	ω
scan width (deg)	1.00	1.00
Θ_{max} (deg)	45.0	44.9
no. reflections recorded	3238	2845
no. non-equiv reflns recorded	2168	2816
R_{merg} (on I)	0.036	0.012
no. reflections retained, I > 2.5σ(I)	1631	2093
no. parameters refined	110	173
R; R_w[a]	0.031; 0.038	0.032; 0.036
goodness of fit[b]	1.13	1.07
max shift / esd. in final least-squares cycle	0.00	0.00
final max, min $\Delta\rho$, e/Å^3	0.600; -0.650	0.820; -0.680

[a]$R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; $R_w = [\Sigma w(|Fo|-|Fc|)^2/\Sigma w|F_o|^2]^{1/2}$.

[b]Goodness-of-fit = $[\Sigma w\Delta^2/(N_{observations} - N_{parameters})]^{1/2}$.

Table 2. Interatomic Distances (Å) and Angles (degrees) for $I_2\overline{GaAs(SiMe_3)_2Ga(I)_2P}(SiMe_3)_2$ (**1**), with Estimated Standard Deviations in Parentheses.

Bond Lengths

Ga(1)-I(1)	2.5555(12)	As/P-Si(2)	2.346(3)
Ga(1)-I(2)	2.5457(11)	Si(1)-C(11)	1.859(9)
Ga(1)-As/P	2.4400(14)	Si(1)-C(12)	1.865(11)
Ga(1)-As/P(a)	2.4422(16)	Si(1)-C(13)	1.837(10)
As/P-Ga(1a)	2.4422(16)	Si(2)-C(21)	1.845(11)
As/P-As/P(a)	3.5189(24)	Si(2)-C(22)	1.860(9)
As/P-Si(1)	2.339(3)	Si(2)-C(23)	1.856(10)

Bond Angles

I(1)-Ga(1)-I(2)	104.27(4)	As/P(a)-As/P-Si(2)	123.27(8)
I(1)-Ga(1)-As/P	114.43(5)	Si(1)-As/P-Si(2)	112.41(10)
I(1)-Ga(1)-As/P(a)	116.25(5)	As/P-Si(1)-C(11)	105.6(3)
I(2)-Ga(1)-As/P	116.74(5)	As/P-Si(1)-C(12)	108.0(3)
I(2)-Ga(1)-As/P(a)	113.33(5)	As/P-Si(1)-C(13)	109.2(3)
As/P-Ga(1)-As/P(a)	92.23(5)	C(11)-Si(1)-C(12)	112.4(4)
Ga(1)-As/P-Ga(1a)	87.77(5)	C(11)-Si(1)-C(13)	112.5(5)
Ga(1)-As/P-As/P(a)	43.91(4)	C(12)-Si(1)-C(13)	108.9(5)
Ga(1)-As/P-Si(1)	116.12(8)	As/P-Si(2)-C(21)	106.4(4)
Ga(1)-As/P-Si(2)	113.64(8)	As/P-Si(2)-C(22)	108.2(4)
Ga(1a)-As/P-As/P(a)	43.86(3)	As/P-Si(2)-C(23)	108.8(3)
Ga(1a)-As/P-Si(1)	111.73(9)	C(21)-Si(2)-C(22)	111.2(5)
Ga(1a)-As/P-Si(2)	112.93(8)	C(21)-Si(2)-C(23)	111.4(5)
As/P(a)-As/P-Si(1)	124.21(9)	C(22)-Si(2)-C(23)	110.6(4)

Table 3. Selected Interatomic Distances (Å) and Angles (degrees) for $[I_2GaP(SiMe_3)_2]_2$ (**3**), with Estimated Standard Deviations in Parentheses.

Bond Lengths

Ga(1)-P(1)	2.394(3)	Si(1)-C(11)	1.847(9)
Ga(1)-P(1a)	2.3995(24)	Si(1)-C(12)	1.864(10)
Ga(1)-I(1)	2.5554(21)	Si(1)-C(13)	12.868(9)
Ga(1)-I(2)	2.5506(13)	Si(2)-C(21)	1.865(9)
P(1)-Ga(1a)	2.3995(24)	Si(2)-C(22)	1.854(10)
P(1)-Si(1)	2.291(3)	Si(2)-C(23)	1.845(9)
P(1)-Si(2)	2.297(3)		

Bond Angles

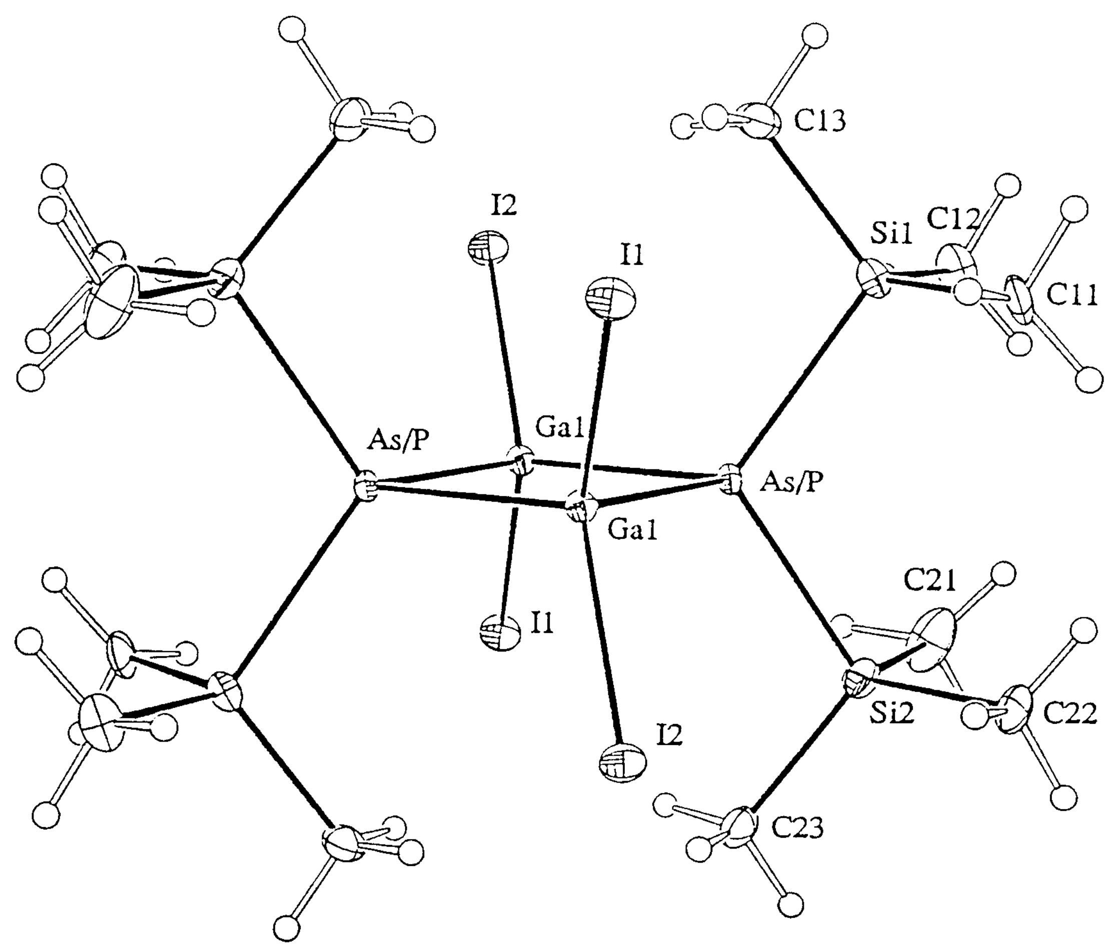
P(1)-Ga(1)-P(1a)	92.19(8)	Ga(1a)-P(1)-Si(1)	115.62(10)
P(1)-Ga(1)-I(1)	116.23(8)	Ga(1a)-P(1)-Si(2)	112.61(11)
P(1)-Ga(1)-I(2)	113.33(7)	Si(1)-P(1)-Si(2)	110.86(13)
P(1a)-Ga(1)-I(1)	114.03(6)	P(1)-Si(1)-C(11)	107.5(3)
P(1a)-Ga(1)-I(2)	116.93(6)	P(1)-Si(1)-C(12)	107.9(3)
I(1)-Ga(1)-I(2)	104.50(6)	P(1)-Si(1)-C(13)	107.3(3)
Ga(1)-P(1)-Ga(1a)	87.81(7)	P(1)-Si(2)-C(21)	110.0(3)
Ga(1)-P(1)-Si(1)	112.76(12)	P(1)-Si(2)-C(22)	106.4(3)
Ga(1)-P(1)-Si(2)	115.56(11)	P(1)-Si(2)-C(23)	114.5(4)

Figure 1. ORTEP diagram showing the solid-state structure of $I_2\overline{GaAs(SiMe_3)_2Ga(I)_2P}(SiMe_3)_2$ (**1**), with thermal ellipsoids at the 30% level.

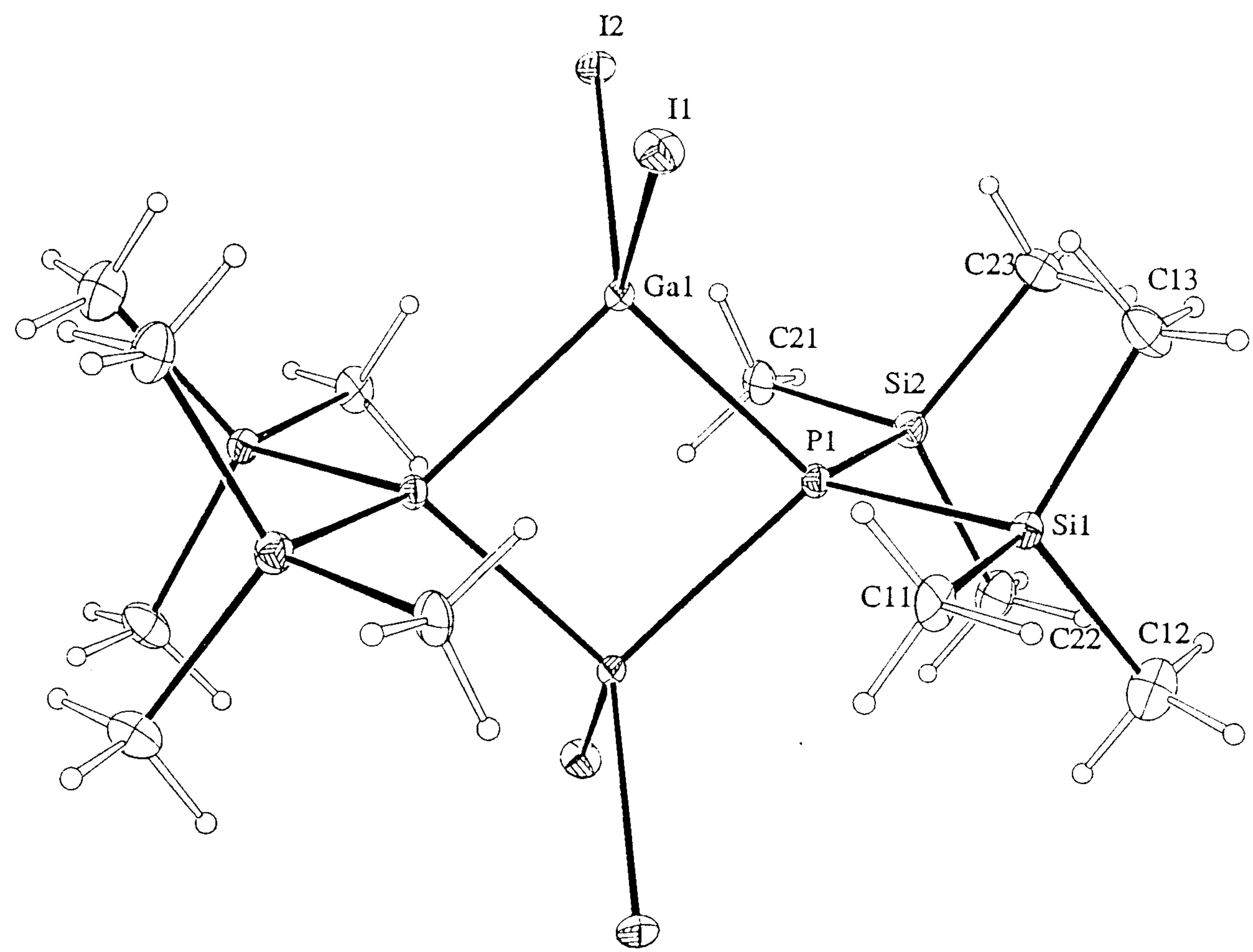
Figure 2. ORTEP diagram showing the solid-state structure of $[I_2GaP(SiMe_3)_2]_2$ (**3**), with thermal ellipsoids at the 30% level.

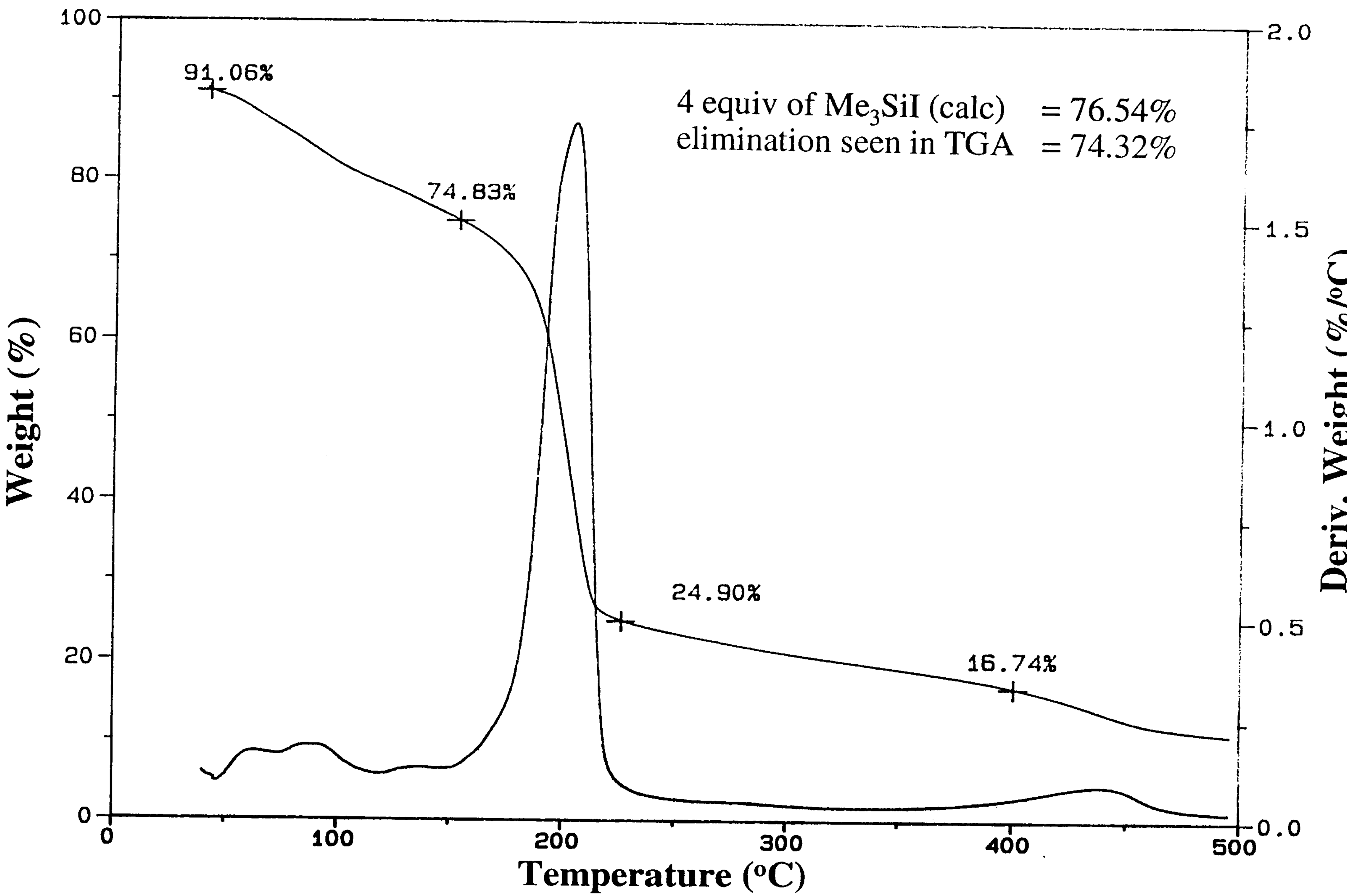
Figure 3. TGA/DTA spectrum of the decomposition of **1**. The sample was heated under dynamic vacuum conditions.

Figure 4. XRD spectrum of product remaining after the thermal decomposition of **1**.



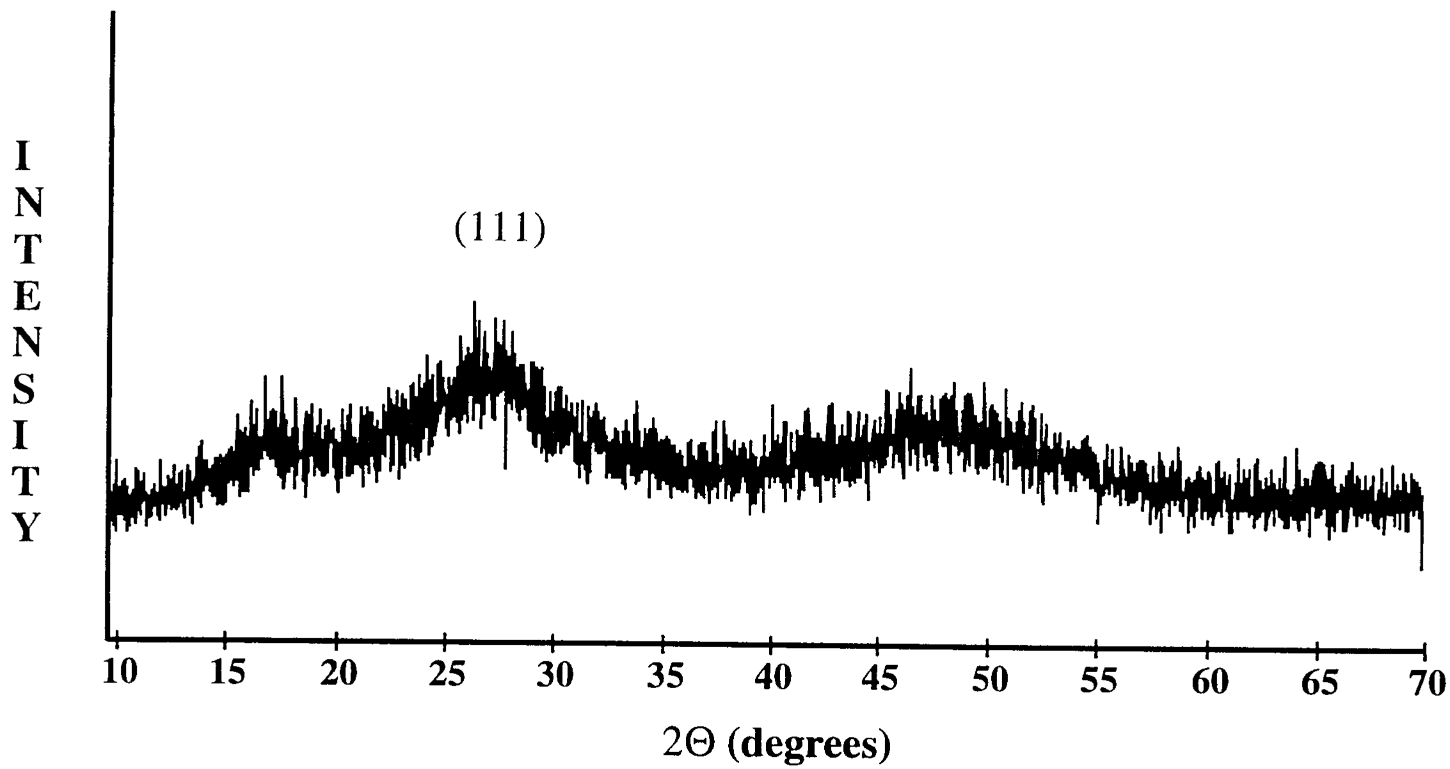
C13
I2
Si1
C12
I1
C11
As/P
Ga1
As/P
Ga1
C21
I1
Si2
C22
I2
C23


I2
I1
Ga1
C21
C23
C13
Si2
P1
Si1
C11
C22
C12



91.06%
74.83%
24.90%
16.74%
4 equiv of Me_3SiI (calc) = 76.54%
elimination seen in TGA = 74.32%
Weight (%)
Deriv. Weight (%/°C)
Temperature (°C)
0
20
40
60
80
100
0
100
200
300
400
500
0.0
0.5
1.0
1.5
2.0

Fig 4



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